

PCT

WORLD INTELLECTUAL PROPERTY
International Bu



INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606153A2

(51) International Patent Classification 6: C11D 3/00		A2	(11) International Publication Number: WO 96/06153 (43) International Publication Date: 29 February 1996 (29.02.96)
(21) International Application Number: PCT/EP95/03211 (22) International Filing Date: 14 August 1995 (14.08.95) (30) Priority Data: 2611/94-8 25 August 1994 (25.08.94) CH		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>Without international search report and to be republished upon receipt of that report.</i>	
(71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): MOLDOVANYI, Laszlo [CH/CH]; Oberer Batterieweg 15, CH-4059 Basle (CH). (74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).			
(54) Title: SURFACE-ACTIVE FORMULATIONS			
(57) Abstract <p>The invention relates to surface-active soap formulations, comprising: (a) 0.01 to 5 % by weight of a microbicidal active substance selected from the group consisting of (a₁) phenol derivatives (a₂) diphenyl compounds (a₃) benzyl alcohols (a₄) chlorhexidine (a₅) C₁₂-C₁₈alkylbetaines and C₈-C₁₈fatty acid amidoalkylbetaines (a₆) amphoteric surfactants and (a₇) trihalocarbonilides; (b) 0.1 to 25 % by weight of one or more than one hydrotropic agent; (c) 0 to 10 % by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances; (d) 0 to 8 % by weight of a salt of a saturated and/or unsaturated C₈-C₂₂fatty acid; (e) 0 to 50 % by weight of a dihydric alcohol; (f) 0 to 70 % by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and (g) mains water or deionised water to make up 100 %, with the proviso that the formulations contain at least one of components (c) and (d). The formulations are used for the disinfection and cleansing of the human skin and hands and of hard objects.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Surface-active formulations

It is commonly knowledge that the antimicrobial/microbicidal properties of active substances in aqueous solutions of soaps or surfactants are strongly influenced by micell systems and may even be almost totally blocked.

Surprisingly, it has now been found that certain hydrotropic suppress the microbicidal inhibiting activity of the micells of soap and surfactant systems (so-called "deblocked surfactant systems"). Accordingly, the antimicrobial/microbicidal activity of different active ingredients can be significantly enhanced in many surfactant systems.

The novel surface-active surfactant formulations comprise

- (a) 0.01 to 5% by weight of a microbicidal active substance selected from the group consisting of
 - (a₁) phenol derivatives,
 - (a₂) diphenyl compounds,
 - (a₃) benzyl alcohols,
 - (a₄) chlorohexidine,
 - (a₅) C₁₂-C₁₄alkylbetaines and C₈-C₁₈fatty acid amidoalkylbetaines,
 - (a₆) amphoteric surfactants,
 - (a₇) trihalocarbanilides, and
 - (a₈) quaternary ammonium salts;
- (b) 0.1 to 25% by weight of one or more than one hydrotropic agent;
- (c) 0 to 10% by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances;
- (d) 0 to 8% by weight of a salt of a saturated and/or unsaturated C₈-C₂₂fatty acid;
- (e) 0 to 50% by weight of a dihydric alcohol;
- (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
- (g) mains water or deionised water to make up 100%,
with the proviso that the formulations contain at least one of components (c) and (d).

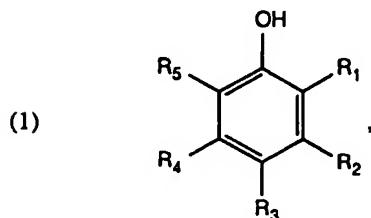
Soap formulations will be understood as meaning aqueous soap solutions which may be obtained as soap or so-called syndet solutions (= synthetic detergents).

The antimicrobial activity of the deblocked surfactant systems reaches upon gram-positive

- 2 -

and gram-negative bacteria as well as yeasts, dermatophytes and the like.

The compounds of component (a₁) preferably correspond to the general formula



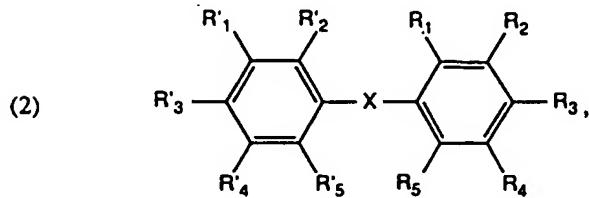
wherein

- R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl oder benzyl,
- R₂ is hydrogen, hydroxy, C₁-C₆alkyl or halogen,
- R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,
- R₄ is hydrogen or methyl,
- R₅ is hydrogen or nitro.

Halogen is bromo or, preferably, chloro.

Such compounds are typically chlorophenols (o-, m-, p-chlorophenols), 2,4-dichlorophenol, p-nitrophenol, picric acid, xylenol, p-chloro-m-xyleneol, cresols (o-, m-, p-cresols), p-chloro-m-cresol, pyrocatechin, resorcinol, orcinol, 4-n-hexylresorcinol, pyrogallol, phloroglucine, carvacrol, thymol, p-chlorothymol, o-phenylphenol, o-benzylphenol, p-chloro-o-benzylphenol and 4-phenolsulfonic acid.

The compounds of component (a₂) preferably correspond to the general formula



wherein

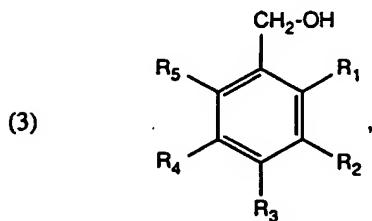
X is sulfur or the methylene group,

R_1 and R'_1 are hydroxy, and

R_2 , R'_2 , R_3 , R'_3 , R_4 , R'_4 , R_5 and R'_5 are each independently of one another hydrogen or halogen.

Typical examples of compounds of formula (2) are hexachlorophene, tetrachlorophene, dichlorophene, 2,3-dihydroxy-5,5'-dichlorodiphenylsulfide, 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenylsulfide, 2,2'-dihydroxy-3,3',5,5',6,6'-hexachlorodiphenylsulfide and 3,3'-dibromo-5,5'-dichloro-2,2'-dihydroxydiphenylamine.

The compounds of component (a₃) preferably correspond to the general formula



wherein

R_1 , R_2 , R_3 , R_4 and R_5 are each independently of one another hydrogen or chloro.

Illustrative examples of compounds of formula (3) are benzyl alcohol, 2,4-, 3,5- or 2,6-dichlorobenzyl alcohol and trichlorobenzyl alcohol.

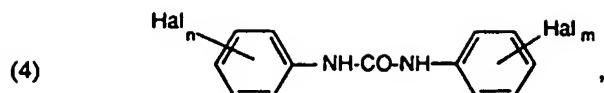
Component (a₄) is chlorohexidine and salts thereof together with organic and inorganic acids, which type of compound may preferably be incorporated into syndet systems.

Component (a₅) is typically C₈-C₁₈cocamidopropylbetaine.

Amphoteric surfactants corresponding to component (a₆) are suitably C₁₂alkylaminocarboxylic and C₁-C₃alkanecarboxylic acids such as alkylaminoacetates or alkylaminopropionates.

The compounds of component (a₇) preferably correspond to the general formula

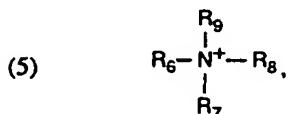
- 4 -



wherein

Hal is chloro or bromo,
n and m are 1 or 2, and
n + m are 3.

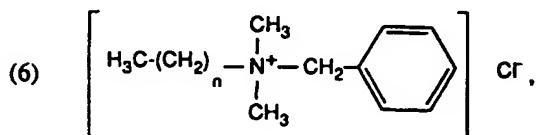
The quaternary ammonium salts of component (a₈) preferably correspond to formula



wherein

R₆, R₇, R₈ and R₉ are each independently of one another C₁-C₁₈alkyl, C₁-C₁₈alkoxy or phenyl-lower alkyl, and
Hal is chloro or bromo.

Among these salts, the compound of formula



wherein

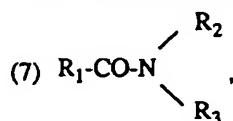
n is an integer from 7 to 17, is very particularly preferred.

The following compounds are suitable for use as component (b):

- (b₁): sulfonates, preferably the salts thereof of terpenoids, or mono- or binuclear aromatic compounds, typically sulfonates of camphor, toluene, xylene, cumene or naphthene;
- (b₂): saturated or unsaturated C₃-C₁₂di- or polycarboxylic acids, typically malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, undecanedicarboxylic acid and dodecanedicarboxylic acid, fumaric, maleic, tartaric

and malic acid as well as citric and aconitic acid;

- (b₃):
- aliphatic saturated or unsaturated C₁-C₁₁monocarboxylic acids, typically acetic, propionic, hexanoic, capric or undecylenoic acid;
- saturated or unsaturated C₃-C₁₂di- or polycarboxylic acids, typically malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, undecanecarboxylic and dodecanedicarboxylic acid, fumaric, maleic, tartaric and malic acid as well as citric and aconitic acid;
- aminocarboxylic acids, typically ethylenediaminetetracetic acid, hydroxyethyl-ethylenediaminetetracetic acid and nitrilotriacetic acid;
- cycloaliphatic carboxylic acids such as camphoric acid;
- aromatic carboxylic acids, typically benzyl, phenylacetic, phenoxyacetic and cinnamic acid, 2-, 3- and 4-hydroxybenzoic acid, anilinic acid as well as o-, m- and p-chlorophenylacetic acid and o-, m- and p-chlorophenoxyacetic acid;
- alkali metal salts and amine salts of inorganic acids, typically the sodium or potassium salts and amine(R₁R₂R₃) salts of hydrochloric, sulfuric, phosphoric, C₁-C₁₀alkylphosphoric acid and boric acid, in which amine salts R₁, R₂ and R₃ have the meaning indicated above;
- isethionic acid;
- tannic acid;
- acid amides of formula

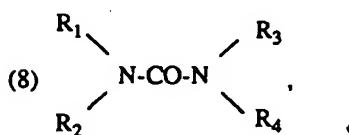


wherein

R₁ is hydrogen or C₁-C₁₂alkyl, and

R₂ and R₃ are each independently of the other hydrogen, C₁-C₁₂alkyl, C₂-C₁₂alkenyl, C₁-C₁₂hydroxyalkenyl, C₂-C₁₂hydroxyalkyl, or a polyglycol ether chain containing 1 to 30 -CH₂-CH₂-O- or -CHY₁-CHY₂-O- groups, wherein Y₁ or Y₂ is a hydrogen radical and the other is methyl, e.g. N-methylacetamide;

- urea derivatives of formula

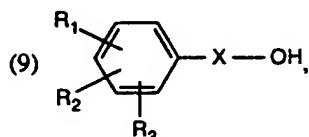


- 6 -

wherein

R₁, R₂, R₃ and R₄ are each independently of one another hydrogen, C₁-C₈alkyl, C₂-C₈alkenyl, C₁-C₈hydroxyalkyl or C₂-C₈hydroxyalkenyl;

- monohydric C₄-C₁₈aliphatic and monocyclic alcohols, typically C₂-C₁₈alkanols, C₂-C₁₈alkenols and terpene alcohols e.g. ethanol, propanol, isopropanol, hexanol, cis-3-hexen-1-ol, trans-2-hexen-1-ol, 1-octen-3-ol, heptanol, octanol, trans-2-cis-6-nonadien-1-ol, decanol, linalol, geraniol, dihydroterpineol, myrcenol, nopol and terpineol;
- aromatic alcohols of formula



wherein

X is -(CH₂)₁₋₆, -CH=CH-CH₂-, or -O-(CH₂)₂₋₆, and
R₁, R₂ and R₃ are each independently of one another hydrogen, hydroxy, halogen or C₁-C₈alkoxy, typically benzyl alcohol, 2,4-dichlorobenzyl alcohol, phenoxyethanol, 1-phenoxy-2-propanol (phenoxyisopropanol) and cinnamyl alcohol;
- polyhydric alcohols and polyhydric alkoxylated, preferably ethoxylated and/or propoxylated alcohols as well as the ethers and esters thereof of the general formula

(10) R₁-O-X-O-R₂,

wherein

R₁ and R₂ are each independently of the other hydrogen, C₁-C₁₂alkyl, C₂-C₁₂alkenyl, C₁-C₈alkanoyl, C₃-C₁₈alkenoyl, R₃-(OCH-CH₂)₁₋₅₀, wherein

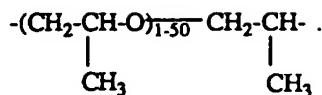


R₃ is hydrogen, C₁-C₁₂alkyl or C₂-C₁₂alkenyl, and

R₄ is hydrogen or -CH₃, and

X is C₂-C₁₀alkylene or C₂-C₁₀alkenylene, -(CH₂CH₂O)₁₋₅₀CH₂-CH₂- or

- 7 -



All organic acids mentioned under (b) may also be obtained in the form of their water-soluble salts, such as the alkali metal salts, preferably the sodium or potassium salts or the amine(NR₁R₂R₃) salts, wherein

R₁, R₂ and R₃ are each independently of one another hydrogen, C₁-C₈alkyl, C₂-C₈alkenyl, C₁-C₈hydroxyalkyl, C₅-C₈cycloalkyl or polyalkylenoxy-C₁-C₁₈alkyl, or

R₁, R₂ and R₃, together with the linking nitrogen atom, are unsubstituted or C₁-C₄alkyl-substituted morpholino.

Component (b) can consist of only one compound of subclass (b₁) or also of mixtures of one or more than one compound of subclass (b₁), also together with components of further subclasses.

A special antimicrobial activity is achieved with a combination of one or more than one compound of subclass (b₁) and one or more than one compound of subclass b₂.

Particularly preferred in this connection is a combination of cumene sulfonate and citric acid monohydrate.

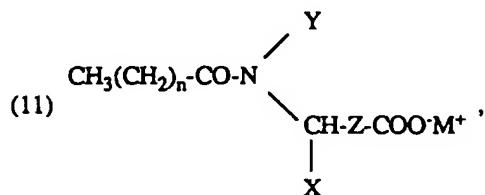
Suitable components (c) are anionic, nonionic or zwitterionic and amphoteric synthetic, surface-active substances.

Suitable anionic surface-active substances are:

- sulfates, typically fatty alcohol sulfates, which contain 8 to 18 carbon atoms in the alkyl chain, e.g. sulfated lauryl alcohol;
- C₈-C₂₂fatty alcohol ether sulfates, typically the acid esters or the salts thereof of a polyadduct of 2 to 30 mol of ethylene oxide with 1 mol of a C₈-C₂₂fatty alcohol;
- the alkali metal salts, ammonium salts or amine salts of C₈-C₂₀fatty acids, which are termed soaps, typically coconut fatty acid;
- alkylamide sulfates;
- alkylamide ether sulfates;
- alkylaryl polyether sulfates;
- monoglyceride sulfates;

- 8 -

- alkane sulfonates, containing 8 to 20 carbon atoms in the alkyl chain, e.g. dodecyl sulfonate;
- alkylamide sulfonates;
- alkylaryl sulfonates;
- α -olefin sulfonates;
- sulfosuccinic acid derivatives, typically alkyl sulfosuccinates, alkyl ether sulfosuccinates or alkyl sulfosuccinamide derivatives;
- N-[alkylamidoalkyl]amino acids of formula



wherein

X is hydrogen, C₁-C₄alkyl or -COO⁻M⁺,

Y is hydrogen or C₁-C₄alkyl,

Z is -(CH₂)_{m₁-1},

m₁ is 1 to 5,

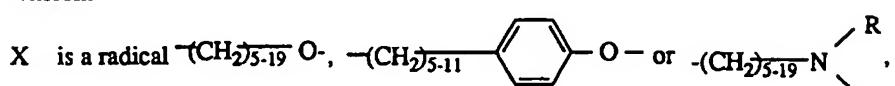
n is an integer from 6 to 18, and

M is an alkali metal ion or an amine ion;

- alkyl ether carboxylates and alkylaryl ether carboxylates of formula

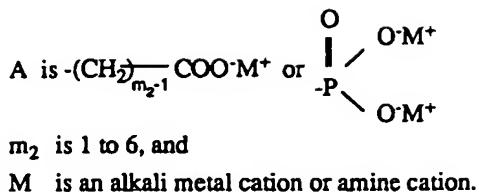


wherein



R is hydrogen or C₁-C₄alkyl,

Y is -(CHCHO)₁₋₅₀-,



The anionic surfactants used may furthermore be fatty acid methyl taurides, alkylisothionates, fatty acid polypeptide condensates and fatty alcohol phosphoric acid esters. The alkyl radicals in these compounds preferably contain 8 to 24 carbon atoms.

The fatty alcohols which may be present in the above-mentioned surfactants are those containing 8 to 22, preferably 8 to 18 carbon atoms, typically octyl, decyl, lauryl, tridecyl, miristyl, cetyl, stearyl, oleyl, arachidyl or behenyl alcohol.

The anionic surfactants are usually obtained in the form of their water-soluble salts, such as the alkali metal, ammonium or amine salts. Typical examples of such salts are lithium, sodium, potassium, ammonium, triethylamine, ethanolamine, diethanolamine or triethanolamine salts. It is preferred to use the sodium or potassium salts or the ammonium-(NR₁R₂R₃) salts, wherein R₁, R₂ and R₃ are each independently of one another hydrogen, C₁-C₄alkyl or C₁-C₄hydroxyalkyl.

The anionic surfactants preferably used in the formulation of this invention are C₈-C₂₂fatty acid alcohol ether sulfates, more particularly the alkali metal salts of lauryl ether sulfate.

Very particularly preferred anionic surfactants in the novel formulation are monoethanolamine lauryl sulfate or the alkali metal salts of fatty alcohol sulfates, preferably the sodium lauryl sulfate and the reaction product of 2 to 4 mol of ethylene oxide and sodium lauryl ether sulfate.

Suitable zwitterionic and amphoteric surfactants are C₈-C₁₈betaines, C₈-C₁₈sulfobetaines, C₈-C₂₄alkylamido-C₁-C₄alkylenebetaines, imidazoline carboxylates, alkylamphocarboxy carboxylic acids, alkylamphocarboxylic acids (e.g. lauroamphoglycinate) and N-alkyl-β-aminopropionates or N-alkyl-β-iminodipropionates. It is preferred to use the C₁₀-C₂₀alkylamido-C₁-C₄alkylenebetaines and, more particularly,

cocoamidopropylbetaine.

Nonionic surfactants are typically derivatives of the adducts of propylene oxide/ethylene oxide having a molecular weight of 1000 to 15000, fatty alcohol ethoxylates (1-50 EO), alkylphenol polyglycol ethers (1-50 EO), ethoxylated carbohydrates, fatty acid glycol partial esters, typically diethylene glycol monstearate, fatty acid alkanolamides and fatty acid dialkanolamides, fatty acid alkanolamide ethoxylates and fatty acid amine oxides. The fatty acid alkanolamides and fatty acid dialkanolamides and, preferably, cocodiethanolamide are to be particularly highlighted.

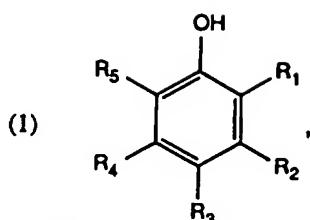
Suitable components (d) are the salts of saturated and unsaturated C₁₂-C₂₂fatty acids, typically lauric, myristic, palmitic, stearic, arachic, behenic, dodecenoic, octadecenoic, oleic, eicosanic and erucic acid, as well as the technical mixtures of such acids, typically coconut fatty acid which is preferably used in the novel formulation. These acids may be obtained in the form of salts, suitable cations being alkali metal cations such as sodium and potassium cations, metal atoms such as zinc atoms and aluminium atoms or nitrogen-containing organic compounds of sufficient alkalinity, typically amines or ethoxylated amines. These salt can also be prepared in situ. Component (d) can also be a mixture of the indicated salts.

Suitable components (e) are dihydric alcohols, preferably those containing 2 to 6 carbon atoms in the alkylene radical, typically ethylene glycol, 1,2- or 1,3-propanediol, 1,3-, 1,4- or 2,3-butanediol, 1,5-pentanediol and 1,6-hexanediol. 1,2-propanediol (propylene glycol) is preferred.

Component (f) is preferably ethanol, n-propanol and isopropanol or a mixture of these alcohols.

Preferred novel formulations are those comprising

(a₁) a compound of formula



wherein

- R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl or benzyl,
- R₂ is hydrogen, hydroxy, C₁-C₆alkyl or chloro,
- R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,
- R₄ is hydrogen or methyl, and
- R₅ is hydrogen or nitro,

- (b) 0.1 to 25% by weight of a mixture of sodium cumene sulfonate and citric acid monohydrate,
- (c) 1 to 10% by weight of a C₈-C₂₂fatty acid alcohol ether sulfate,
- (e) 0 to 50% by weight of a dihydric alcohol;
- (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
- (g) mains water or deionised water to make up 100%.

The pH of the novel formulation is 3 to 10, preferably 4.5 to 6.

The novel formulations obtained as soap or syndet solutions may additionally comprise customary additives, typically sequestrants, dyes, perfume oils, thickeners or solidifiers (consistency regulators), emollients, UV absorbers, skin-protection agents, antioxidants, additives which improve the mechanical properties, such as dicarboxylic acids and/or Al, Zn, Ca, Mg salts of C₁₄-C₂₂fatty acids and, if desired, preservatives.

The novel soap bars can be fabricated in per se known manner, typically by mixing the novel components (a) and (b) and, optionally, (c), (d), (e) and (f), as well as any additives in a jerk mixer at 18-25°C. After the composition obtained has been processed, it is extruded at 40 to 60°, preferably from 45 to 50°C, and then cut and stamped in moulds.

Soap formulations of the invention can be prepared by mixing components (a) and (b) and, optionally, (c), (d), (e) and (f), in any order, with the requisite amount of water and stirring

the mixture to homogeneity. The mixture is bulked to 100% with additional water. This procedure is a purely physical procedure. Accordingly, there is no chemical reaction of the individual components.

For disinfection and cleansing of the human skin and hands and of hard objects, the novel soap formulations can be applied thereto in dilute or undilute form, suitably in an amount of at least 2 ml, preferably in the undilute form, for hand disinfection.

The invention is illustrated by the following Examples. Parts and percentages are by weight.

Example 1:

1.0 part o-phenylphenol,
4.0 parts sodium lauryl ether-2-sulfate,
8.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 2:

1.0 part o-phenylphenol,
4.0 parts sodium lauryl ether-4-sulfate,
8.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

is stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 3:

1.0 part p-chloro-m-xylene,
4.0 parts sodium lauryl ether-2-sulfate
8.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are mixed to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 4:

1.0 part p-chloro-o-benzylphenol,
4.0 parts sodium lauryl ether-2-sulfate
8.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 5:

2.0 parts benzyl alcohol,
4.0 parts sodium lauryl sulfate
5.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 6:

4.0 parts cocamidopropylbetaine,
5.0 parts sodium cumene sulfonate,
10.0 parts propylene glycol,
8.0 parts citric acid monohydrate, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 7:

4.0 parts cocamidopropylbetaine,
12.0 parts ethanol,
8.0 parts citric acid monohydrate, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 8:

4.0 parts sodium lauraminopropionate,
5.0 parts sodium cumene sulfonate,
10.0 parts propylene glycol,
8.0 parts citric acid monohydrate, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 9:

4.0 parts sodium lauraminopropionate,
12.0 parts ethanol,
8.0 parts citric acid monohydrate, and

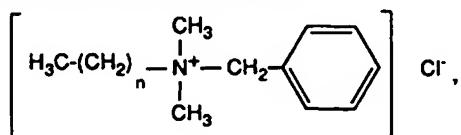
- 15 -

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 10:

1.0 part of the compound of formula



wherein n is an integer from 7 to 17,

4.0 parts cocamidopropylbetaine,

12.0 parts ethanol,

8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 11:

1.0 part 2,4-dichlorobenzyl alcohol

4.0 parts sodium laurylsulfate,

5.0 parts sodium cumene sulfonate,

1.0 part propylene glycol,

8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 12: Test of the microbicidal activity of the novel formulations

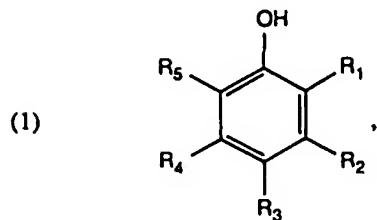
The microbicidal activity (in decimal logarithms) of the novel formulations according to Examples 1 to 11 is determined with a suspension test. This test is used to assess the bactericidal activity of water-soluble antiseptics, disinfectants and of liquid soaps. The test consists in seeding the test product in selected dilutions with the test bacillus. After a certain contact time, aliquots are taken and the number of surviving bacilli is determined. The difference between the number of the bacilli added and the number of the surviving bacilli is expressed as bacilli reduction in decimal logarithms. The concentration is 90%, the contact time is 30 seconds.

The following test bacilli are used:

<u>Example</u>	Staph. aureus ATCC 9144	Strept. faecalis ATCC 10,541	E. Coli ATCC 10,536	P.aeruginosa CIP A-22	Serratia marcescens ATCC 13,880
1	4.6	>5.1	>5.3	>5.3	>5.4
2	>5.5	>5.2	>5.1	>5.3	>5.5
3	>5.5	>5.2	>5.1	>5.3	>5.5
4	>5.5	>5.2	>5.1	>5.3	>5.5
5	>6	>6	>6	>6	>6
6	2.0	0.2	1.4	>6	2.7
7	0	0.5	2.6	>6	1.3
8	0.1	0.3	0.7	>6	2.5
9	3.5	>6	>6	>6	4.2
10	1.0	1.7	>6	>6	4.7
11	3.4	>6	>6	>6	>6

What is claimed is**1. A surface-active surfactant formulation, comprising**

- (a) 0.01 to 5% by weight of a microbicidal active substance selected from the group consisting of
 - (a₁) phenol derivatives,
 - (a₂) diphenyl compounds,
 - (a₃) benzyl alcohols,
 - (a₄) chlorohexidine,
 - (a₅) C₁₂-C₁₄alkylbetaines and C₈-C₁₈fatty acid amidoalkylbetaines,
 - (a₆) amphoteric surfactants,
 - (a₇) trihalocarbanilides, and
 - (a₈) quaternary ammonium salts;
 - (b) 0.1 to 25% by weight of one or more than one hydrotropic agent;
 - (c) 0 to 10% by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances;
 - (d) 0 to 8% by weight of a salt of a saturated and/or unsaturated C₈-C₂₂fatty acid;
 - (e) 0 to 50% by weight of a dihydric alcohol;
 - (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
 - (g) mains water or deionised water to make up 100%,
- with the proviso that said formulations contain at least one of components (c) and (d).

2. A formulation according to claim 1, wherein the compounds used for component (a₁) are those of the general formula

wherein

R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl oder benzyl,

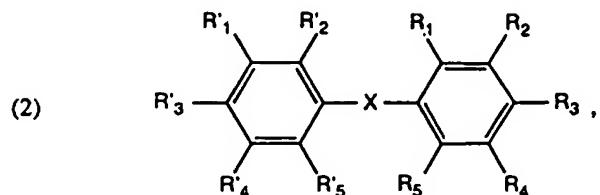
R₂ is hydrogen, hydroxy, C₁-C₆alkyl or halogen,

R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the

- 18 -

- alkali metal salts or ammonium salts thereof,
R₄ is hydrogen or methyl,
R₅ is hydrogen or nitro.

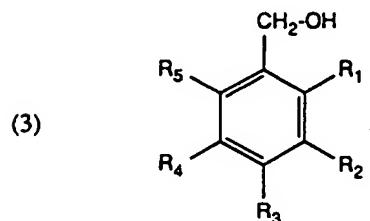
3. A formulation according to claim 1, wherein the compounds used for component (a₂) are those of formula



wherein

- X is sulfur or the methylene group,
R₁ and **R'**₁ are hydroxy, and
R₂, **R'**₂, **R**₃, **R'**₃, **R**₄, **R'**₄, **R**₅ and **R'**₅ are each independently of one another hydrogen or halogen.

4. A formulation according to claim 1, wherein the compounds used for component (a₃) are those of formula



wherein

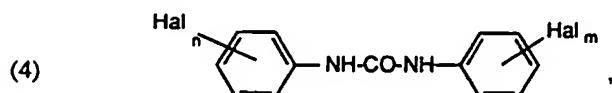
- R**₁, **R**₂, **R**₃, **R**₄ and **R**₅ are each independently of one another hydrogen or chloro.

5. A formulation according to claim 1, wherein component (a₄) is chlorohexidine or a salt thereof with an organic or inorganic acid.

6. A formulation according to claim 1, wherein component (a₅) is cocamidopropylbetaine.

7. A formulation according to claim 1, wherein component (a₆) is a C₁₂alkylaminocarboxylic acid or a C₁-C₃alkanecarboxylic acid.

8. A formulation according to claim 1, wherein the compounds used for component (a₇) are those of the general formula



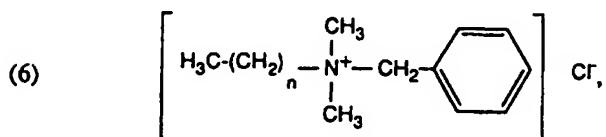
wherein

Hal is chloro or bromo,

n and m are 1 or 2, and

n + m are 3.

9. A formulation according to claim 1, wherein the compound used for component (a₈) is a compound of formula



wherein

n is an integer from 7 to 17.

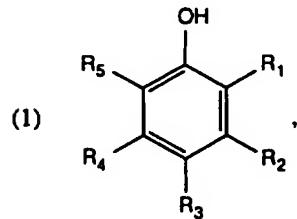
10. A formulation according to any one of claims 1 to 9, wherein component (b₁) is a sulfonate, preferably a salt thereof of a terpenoid or of a mono- or binuclear aromatic compound.

11. A formulation according to claim 10, wherein the mono- or binuclear aromatic compounds are the sulfonates of camphor, toluene, xylene, cumene or naphthalene.

12. A formulation according to any one of claims 1 to 11, wherein component (b) consists of only one compound of subclass (b₁) or also of a mixture of one or more than one compound of subclass (b₁) together with components of further subclasses.

- 20 -

13. A formulation according to any one of claims 1 to 11, wherein component (b) is a combination of one or more than one compound of subclass (b₁) and one or more than one compound of subclass (b₂).
14. A formulation according to claim 13, wherein a combination of cumene sulfonate and citric acid monohydrate is used.
15. A formulation according to any one of claims 1 to 14, wherein component (c) is an anionic surfactant in the form of the water-soluble salt thereof.
16. A formulation according to claim 15, wherein component (c) is C₈-C₂₂fatty alcohol ether sulfate.
17. A formulation according to claim 16, wherein component (c) is an alkali metal salt of lauryl ether sulfate.
18. A formulation according to any one of claims 1 to 17, wherein component (d) is selected from the group consisting of lauric, myristic, palmitic, stearic, arachic, behenic, dodecenic, tetradecenic, octadecenic, oleic, eicosenic and erucic acid.
19. A formulation according to any one of claims 1 to 18, wherein component (e) is propylene glycol.
20. A formulation according to any one of claims 1 to 19, wherein component (f) is selected from the group consisting of ethanol, propanol, isopropanol, and mixtures of these alcohols.
21. A surface-active formulation comprising
(a₁) a compound of formula



wherein

- R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl oder benzyl,
- R₂ is hydrogen, hydroxy, C₁-C₆alkyl or halogen,
- R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,
- R₄ is hydrogen or methyl,
- R₅ is hydrogen or nitro,
- (b) 0.1 to 25% by weight of a mixture of sodium cumene sulfonate and citric acid monohydrate,
- (c) 0 to 10% by weight of a C₈-C₂₂fatty alcohol ether sulfate,
- (d) 0 to 50% by weight of a dihydric alcohol,
- (e) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols, and
- (f) mains water or deionised water to make up 100%.

22. Use of an antimicrobial soap formulation as claimed in any one of claims 1 to 21 for the disinfection and cleansing of the human skin and hands and of hard objects.